

Direct-Current Plasma Optical Emission Spectrometry

Direct-current plasma optical emission spectrometry (DCP-OES) allows quantitative determinations of elements at major, minor, and trace levels. The simultaneous determination of up to 20 elements in a single solution sample is possible.

Principle of Technique

A solution to be analyzed is aspirated into a spray chamber where droplets are entrained in an argon gas flow. Larger droplets collide with the chamber walls and are drained away. The aerosol is then swept into a dc plasma created by a continuous arc between two graphite anodes and a tungsten cathode. The sample is desolvated, atomized, and excited by the 4000–6000 K plasma. Light from the plasma is focused onto an echelle spectrometer that disperses light in two dimensions using an echelle grating and a quartz-prism cross disperser. The echelle grating diffracts light with high dispersion in high orders while the prism refracts light with low dispersion to separate the overlapping orders. Intensities from selected emission lines are measured by a bank of photomultipliers placed at the most intense wavelengths for 20 preselected elements of interest. The DCP-OES instrument is occasionally operated in a qualitative mode by visually comparing the lines of all elements excited in the DCP. In this qualitative mode, the echelle spectrum with a template showing the location of the major spectral image is diverted by a folding mirror to a Polaroid film camera. By overlaying the template on the Polaroid image, one can qualitatively map out the elements that are present at high concentrations in a sample.

Samples

Form. Liquids, usually aqueous solutions, can be analyzed as received or after a dilution. Solids require dissolution.

Size. 20 mL of solution is required for routine analysis. Solid quantity depends on analyte and concentration. Typically, samples of sufficient size to provide several μg of analyte are required.

Preparation. Solids must be dissolved in a suitable medium, usually aqueous acid. Organic materials typically require more aggressive treatment, such as high-temperature ashing.

Limitations

Relative accuracy and precision of this technique is 1 to 10%, depending on how well the background matrix is matched.

Solid materials must be dissolved. The multichannel operating mode of the instrument specifies a predetermined group of elements to be analyzed. The method yields no information on chemical speciation or oxidation state.

Estimated Analysis Time Including instrument start-up time, qualitative analysis of a single solution requires about 2 h. Usually 3 to 4 h is needed for preparation of samples and standards for a quantitative analysis.

Examples of Applications

- Determination of metallic impurities in plutonium and its alloys.
- Measurement of regulatory toxic metals in hazardous waste samples.
- Qualitative and semiquantitative element surveys using a photographic plate option.

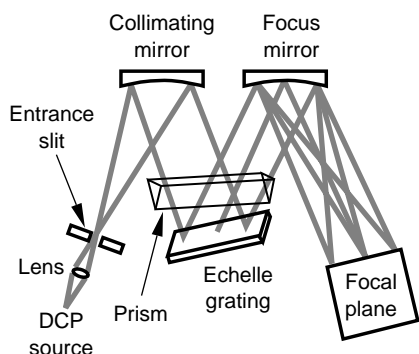
Plutonium sample analysis using a DCP source enclosed in a glove box.

Element	Concentration (wt% in Pu) ^a	Coefficient of variation (%) ^b
Am	0.02–0.08	1.5
Fe	0.05–0.15	2.3
Ga	0.10–1.5	2.0
Np	0.0005–0.005	2.8
Si	0.03–0.07	2.5
Ta	0.002–0.02	4.0
Zr	0.10–0.50	4.5
Rare earths	0.10–0.20	3.5
Trace elements ^c	0.003–0.03	8.6

^a Elements present in plutonium at concentrations >0.1% are determined in dilute Pu solutions, usually 0.04 mg Pu/mL. Elements present in Pu at concentrations <0.1% are usually separated from Pu by ion-exchange chemistry prior to DCP-OES spectrometry.

^b 95% confidence level.

^c Trace elements are aluminum, boron, calcium, chromium, copper, magnesium, manganese, molybdenum, nickel, lead, tin, titanium, vanadium, zinc.



The echelle grating used in DCP-OES improves spectral resolution by a factor of ten over that of related techniques.

Additional time may be required for solid sample dissolution and matrix separation.

Capabilities of Related Techniques

Inductively-coupled-plasma emission spectroscopy (ICP-AES) is closely related, differing in the optics and the type of plasma employed. It generally has somewhat lower limits of detection because of a longer residence time of the analyte in the plasma, a higher plasma temperature, and a more stable plasma. DCP-OES on the other hand, has a higher spectral line resolution because of the echelle spectrometer. It thus may

be less subject to interferences, especially by elements with many spectral lines such as iron and uranium.

Inductively-coupled plasma mass spectrometry (ICP-MS) is also a multi-element technique. It has lower limits of detection for many elements and provides isotopic information.

DC-arc optical emission spectroscopy (DC-arc) and x-ray fluorescence spectrometry may be applicable and can be used to analyze solids directly without dissolution. Atomic absorption spectrometry is a single-element method that may be more accurate and precise for some elements.

The Analytical Chemistry Section operates a DCP-OES instrument in Plutonium Analytical Chemistry, where it is used primarily for the analysis of Pu-bearing materials.

(H)	<div><div>Ag 1</div><div>← Element</div><div>← Typical detection limit using conventional solution nebulization (µg/L)</div></div>																(H)	(He)	
Li 2	Be 0.5											B 5	(C)	(N)	(O)	(F)	(Ne)		
Na 2	Mg 0.1											Al 2	Si 15	P 75	S 5	(Cl)	(Ar)		
K 15	Ca 0.2	Sc 1	Ti 3	V 2	Cr 2	Mn 2	Fe 3	Co 3	Ni 2	Cu 2	Zn 2	Ga 3	Ge 10	As 45	Se 45	(Br)	(Kr)		
Rb 15	Sr 0.3	Y 2	Zr 4	Nb 40	Mo 2	(Tc)	Ru 50	Rh 1	Pd 2	Ag 3	Cd 5	In 20	Sn 25	Sb 45	Te 75	(I)	(Xe)		
(Cs)	Ba 0.5	La 2	Hf 10	Ta 20	W 20	Re 8	Os 20	Ir 20	Pt 30	Au 3	Hg 20	Tl 3	Pb 10	Bi 75	(Po)	(At)	(Rn)		
(Fr)	(Ra)	(Ac)	(Rf)	(Ha)															

Ce 30	Pr 20	Nd 10	(Pm)	Sm 10	Eu 2	Gd 10	Tb 10	Dy 3	Ho 3	Er 10	Tm 3	Yb 1	Lu 1
Th 20	(Pa)	U 40	Np 250	Pu 50	Am 50	(Cm)	(Bk)	(Cf)	(Es)	(Fm)	(Md)	(No)	(Lr)

Typical detection limits using conventional solution nebulization (μg/L). Elements capable of simultaneous determination by DCP-OES are shown in bold.

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